

## CLAIMS

*What is claimed is:*

1. An apparatus for providing a solid precursor to a surface of a work piece via a supercritical solution, the apparatus comprising:
  - a plurality of vessels for housing the solid precursor and allowing it to contact a solvent under supercritical or near supercritical conditions to generate a solution of the solid precursor;
  - a generator recirculation loop in fluid communication with the plurality of vessels and allowing the solution of the solid precursor to recirculate through the plurality of vessels, said solution being under supercritical or near supercritical conditions over its entire recirculation path; and
  - a delivery mechanism adapted to deliver, under supercritical or near supercritical conditions, a portion of the solution to a reactor for housing said work piece;wherein the solid precursor is a solid at or about standard temperature and pressure.
2. The apparatus of claim 1, wherein the solution is a saturated solution.
3. The apparatus of claim 1, wherein the delivery mechanism comprises a plurality of syringe pumps.
4. The apparatus of claim 3, further comprising a dilution mechanism for diluting the saturated solution with said solvent under supercritical or near supercritical conditions to produce a diluted solution of the solid precursor for delivery to the reactor.
5. The apparatus of claim 1, wherein the work piece is a partially fabricated integrated circuit.
6. The apparatus of claim 2, wherein the generator recirculation loop comprises a pump for providing fluid flow and a valve for causing at least some fraction of the

solvent to circulate through the plurality of vessels housing the solid precursor to ensure production of the saturated solution.

7. The apparatus of claim 4, wherein the dilution mechanism also comprises the plurality of syringe pumps.

8. The apparatus of claim 4, wherein the dilution mechanism comprises a source of supercritical solvent for supplying the plurality of syringe pumps.

9. The apparatus of claim 4, further comprising a reactor recirculation loop configured to allow recirculation of the diluted solution through the reactor under supercritical or near supercritical conditions.

10. The apparatus of claim 9, further comprising a first fluid inlet, in fluid communication with the reactor, for supplying supercritical fluids to the reactor; and a first bleed valve, located downstream from the reactor.

11. The apparatus of claim 10, further comprising a by-pass line configured to allow isolation of the reactor from the reactor recirculation loop, thus forming a by-pass recirculation loop.

12. The apparatus of claim 11, further comprising a second fluid inlet, in fluid communication with the by-pass recirculation loop, for supplying supercritical fluid directly to the by-pass recirculation loop.

13. The apparatus of claim 12, wherein the second fluid inlet comprises a secondary feed line which feeds from the first fluid inlet.

14. The apparatus of claim, 13 further comprising a second bleed valve, located downstream from the reactor and the first bleed valve.

15. The apparatus of claim 9, wherein the reactor recirculation loop provides flow of the diluted solution through the reactor at between about 50 and 200ml per minute.

16. The apparatus of claim 1, wherein components of the apparatus comprise at least one of hastalloy, stainless steel, and inconel.

17. A method of forming a layer on a work piece, the method comprising:

(a) providing the work piece to a reactor;

(b) providing a solvent in the reactor under supercritical or near supercritical conditions;

(c) introducing a supercritical solution of a dissolved precursor to the reactor, while maintaining supercritical or near supercritical conditions in the reactor; and

(d) allowing the precursor to form a layer on the work piece;

wherein the precursor is a solid at or about standard temperature and pressure.

18. The method of claim 1, wherein the work piece is a wafer.

19. The method of claim 1, wherein the solvent comprises at least one of carbon dioxide, ammonia, water, ethanol, ethane, propane, butane, pentane, dimethyl ether, hexafluoroethane, and mixtures thereof.

20. The method of claim 1, wherein the layer comprises at least one of a diffusion barrier, a conductive metal, a dielectric, an antireflective, an etch stop, a photoresist, a resistive, and an adhesion-seed layer.

21. The method of claim 20, wherein the diffusion barrier comprises at least one of tantalum, tantalum nitride, titanium, titanium nitride, tungsten, tungsten nitride, cobalt, nickel, indium, tin, platinum, palladium, ruthenium oxide, and ruthenium.

22. The method of claim 20, wherein the dielectric comprises a POSS-material.

23. The method of claim 22, wherein the POSS-material comprises at least one of octavinyl-POSS, methacrylfluoro-3-POSS, and methacrylfluoro-13-POSS.

24. The method of claim 20, wherein the metal comprises at least one of copper, aluminum, gold, silver, aluminum-copper, aluminum-silicon, and aluminum-silicon-copper.
25. The method of claim 24, wherein each of the aluminum-copper, the aluminum-silicon, and the aluminum-silicon-copper contain between about 0.5 and 1% each of copper and silicon.
26. The method of claim 17, further comprising repeating (b)-(d) for a second dissolved precursor to form a second layer on top of the layer.
27. The method of claim 26, wherein the layer is a diffusion barrier and the second layer is a copper layer.
28. The method of claim 27, wherein the dissolved precursor comprises at least one of cobalt(II)acetylacetonate, cobalt(II)tetramethyl-heptadionate, and tantalum(V)tetraethoxide-2,4-pentadionate..
29. The method of claim 27, wherein the second dissolved precursor comprises at least one of copper(II)tetramethylheptadionate, copper(II)trimethyloctanedionate, and copper(II)formate.
30. The method of claim 28, wherein the solvent comprises carbon dioxide.
31. The method of claim 29, wherein the solvent comprises carbon dioxide.
32. The method of claim 17, wherein (b) comprises:  
introducing the solvent under non-supercritical conditions; and  
transitioning to supercritical conditions in the reactor.
33. The method of claim 17, wherein (c) comprises maintaining substantially constant pressure during introduction of the dissolved precursor, to thereby reduce the likelihood that the precursor will precipitate from the solution.

34. The method of claim 17, wherein (c) comprises maintaining substantially constant temperature during introduction of the dissolved precursor.

35. The method of claim 26, wherein the reactor is flushed with a supercritical fluid before repeating (c)-(d) to form the second layer.

36. The method of claim 17, wherein the solution of the dissolved precursor is a dilute solution.

37. The method of claim 36, wherein the dilute solution is made from a saturated solution of the dissolved precursor.

38. The method of claim 37, wherein the saturated solution is formed by allowing a precursor to contact a recirculating flow of the solvent, said solvent being under supercritical or near supercritical conditions over its entire recirculation path.

39. The method of claim 36, wherein the dilute solution is recirculated through the reactor during (b)-(d).